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MONTE CARLO TRAJECTORY CALCULATIONS OF THE THREE-BODY RECOMBINATION AND DISSOCIATION OF DIATOMIC MOLECULES

by

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ABSTRACT

The modified phase-space theory of reaction rates has been applied to the problem of the three-body recombination and dissociation of diatomic molecules. The results illustrate the important influence of the weak attractive minimum in the third-body interaction potential and the effect of barrier penetration for recombination at low temperatures. The system $N_2 + Ar$ was used as a typical illustrative example, and good agreement was obtained between the theoretical predictions and the experimental measurements of the reaction rate coefficients over the temperature range 200-12000 °K.

The recrossing factor and the nonequilibrium factor were obtained from Monte Carlo trajectory calculations for states near the dissociation limit. The trajectories were sampled within the reaction zone, with a weight proportional to the equilibrium reaction rate, and numerically integrated in both timewise directions to determine the complete

histories of the collisions. A simple, separable function for the equilibrium transition rate $R(\varepsilon_i, \varepsilon_f)$ from initial energy states ε_i to final energy states ε_f , which could be characterized by three parameters, was obtained to fit the numerical data and was used to solve the steady-state master equation.

Distributions of the trajectories with respect to energies and impact parameters are presented, and several typical trajectories are shown to illustrate the important features of the collisions. The contribution to the overall reaction rate from the "complex mechanism" was also obtained.

I. INTRODUCTION

The most general theoretical investigation of the problem of three-body recombination and dissociation is that carried out by Keck and his coworkers.¹⁻⁵ This theory is based on a phase space representation and is sufficiently general to include all previous classical theories as special cases. They applied the theory to the three-body recombination and dissociation of diatomic molecules with an inert third-body collision partner (including the $H + H + H_2$ recombination) and obtained good agreement between theory and experiment in general. In addition, their work illustrated the importance of such features as the weak attractive van der Waals forces between the recombining atoms and the inert third-body atoms for recombination at low temperatures, and the effects of electronically excited states and nonequilibrium internal distributions on the overall recombination and dissociation rates.

The steady-state reaction rate coefficient (to be compared with experimental measurements) is obtained as the triple product

$$k = k^B (N/N_0) (k/k_e) \quad (1.1)$$

where k^B is the barrier rate.² The values of recrossing factors (N/N_0) and nonequilibrium factors (k/k_e) used in previous studies³⁻⁵ were deduced using the results of Monte Carlo trajectory calculations^{2,6} and master equation solutions⁷ in which the recombining atoms had similar masses. Also, the third body was considered to be purely repulsive. Results of Monte Carlo trajectory calculations of the dissociation of HCl in Ar have been presented recently⁸ which illustrated the special features of collisions involving highly asymmetric diatomic molecules and the importance of rotational motion in such collisions. Excellent agreement was obtained between the theoretical predictions and the shock-tube measurements of the dissociation rate coefficients of HCl over the temperature range 2500-5000 °K.

In this paper the results of Monte Carlo trajectory calculations are presented for systems which have a weak minimum in the three-body interaction potential, the system N₂ + Ar being used as an illustrative example. We shall not repeat details of the theory and calculations that were already presented in previous publications.¹⁻⁸ Instead, in Section II we shall summarize the interaction potentials used, and in Section III present the important features of the present calculations. The results and their comparison with experiment will be presented in Section IV, and Section V will contain our concluding discussions.

II. INTERACTION POTENTIALS

The interaction potential (V_0) of the three-body system (X-Y-M) was separated into two parts:

$$v_0 = v_{XY} + v_3 \quad (2.1)$$

where v_{XY} is the potential of the recombining atoms ($X - Y$), and v_3 is the potential due to the presence of the third body (M). The Morse potential function

$$V = D \exp[-\beta(r - r_e)] \{ \exp[-\beta(r - r_e)] - 2 \} \quad (2.2)$$

was used to represent v_{XY} . As was done before,^{2,3} the dumbbell model

$$v_3 = v_{XM} \text{ for } r_{XM} < r_{YM}$$

and

(2.3)

$$v_3 = v_{YM} \text{ for } r_{XM} > r_{YM}$$

was assumed for the potential v_3 , and v_{XM} and v_{YM} were represented by the Morse form, Equation (2.1).

The potential parameters for v_{XY} , v_{XM} , and v_{YM} required in the present calculations were determined in the same manner as in previous studies.³⁻⁵ Table I summarizes these parameters.

III. MONTE CARLO TRAJECTORY CALCULATIONS

The principles of the Monte Carlo technique used here have been explained previously,⁸ and a more general discussion may be found in the literature.⁹⁻¹¹ Details of the selection of initial conditions and of the integration of equations of motion are contained in Reference 12. In general, total energy was conserved to within 0.01 kT, and the trajectories were followed in both time-wise directions from the initial point until the condition

$$|v_3| < 0.01 \text{ kT} \text{ and } r_3 > 0 \quad (3.1)$$

was satisfied (r_3 is the distance between the third body M and the center of mass of the molecule XY). However, for studies involving complexes, the alternative cutoff condition

$$|v_{XY}| < 0.01 kT \text{ and } |v_{XM}| < 0.01 kT \text{ and } \dot{r}_1 > 0, \quad (3.2)$$

or

$$|v_{XY}| < 0.01 kT \text{ and } |v_{YM}| < 0.01 kT \text{ and } \dot{r}_2 > 0$$

was also introduced. Here r_1 is the distance between the atom X and the center of mass of Y - M, and r_2 is the distance between the atom Y and the center of mass of X - M.

As was done in Reference 8, the recrossing correction factor (N/N_0) was obtained directly from the results of the trajectory calculations by counting. Also, the "one-way" equilibrium transition rate between energy states $\epsilon = \epsilon_i$ and $\epsilon = \epsilon_f$, per unit volume, per unit initial and final energies, was fitted by the empirical forms

$$R(\epsilon_i, \epsilon_f) = AG(\epsilon_f) \exp(\alpha\epsilon_f - \beta\epsilon_i) \quad (3.3a)$$

and

$$R(\Delta, \bar{\epsilon}) = AG(\bar{\epsilon}) \exp(-a\Delta - b\bar{\epsilon}) \quad (3.3b)$$

where A, α , β , a , b are constants, $G(\cdot)$ is a relatively slowly varying function, Δ is the absolute value of the energy transfer, $\bar{\epsilon}$ is the mean of the initial and final energies, and

$$\alpha = a - b/2, \text{ and } \beta = a + b/2. \quad (3.4)$$

Various moments of the energy transfer with respect to $R(\epsilon_i, \epsilon_f)$ were used in the fitting procedure. In general, the m -th moment is defined as

$$Q_m(\epsilon) \equiv \int_{-\infty}^{\epsilon} \int_{\epsilon}^{\infty} f(\epsilon, \epsilon_i, \epsilon_f) R(\epsilon_i, \epsilon_f) (\epsilon_i - \epsilon_f)^{m-1} s^m d\epsilon_i d\epsilon_f \quad (3.5)$$

where ϵ is the energy of the surface from which samples were taken (defined in Reference 8), $f(\epsilon, \epsilon_i, \epsilon_f)$ is a weighting-normalizing function, and

$$s^m = [(\bar{\epsilon} - \epsilon)/|\bar{\epsilon} - \epsilon|]^m \quad (3.6)$$

determines the sign of the odd moments. The corresponding "absolute" moments $|Q|_m(\epsilon)$, are obtained by setting $S \equiv 1$, and the moments used in this paper $D_m(\epsilon)$, correspond to

$$f(\epsilon, \epsilon_1, \epsilon_f) = G(\epsilon)/G(\epsilon_f) R_v(\epsilon) \quad (3.7)$$

where $R_v(\epsilon)$ is the variational rate for the surface $S(\epsilon)$, defined in References 2 and 8.

Using Equations (3.5), (3.7), and relationships contained in Reference 8 and evaluating the integral by Monte Carlo methods, we obtain

$$D_m(\epsilon) = \sum_{j=1}^{N_0} [G(\epsilon)/G(\epsilon_f)] (x_j/n_j) (\epsilon_1 - \epsilon_f)_j^{m-1} S^m / N_0 \quad (3.8)$$

where $x_j = 1$ if the trajectory is reactive, $x_j = 0$ otherwise, n_j is the number of crossings of that trajectory in the reactive direction, and N_0 is the total number of trajectories sampled on the surface $S(\epsilon)$. This is the equation used in the actual calculation of the moments $D_m(\epsilon)$ from data generated by trajectory calculations.¹³ Furthermore, following the procedures used in Reference 8, we obtain

$$\Lambda/R_v(0) = Ca\beta \quad (3.9)$$

and

$$D_m(\epsilon) = Ca\beta \exp(\epsilon) \int_{-\infty}^{\epsilon} \int_{\epsilon}^{\infty} (\epsilon_1 - \epsilon_f)^{m-1} \exp(\alpha\epsilon_f - \beta\epsilon_1) S^m d\epsilon_1 d\epsilon_f \quad (3.10)$$

which can be evaluated exactly to yield

$$|D|_m(\epsilon) = \begin{cases} (m-1)! [(B^m - A^m)/b(A\beta)^{m-1}] C \exp[(1-b)\epsilon] , & m > 0 ; \\ (A\beta/b) \ln(\beta/A) C \exp[(1-b)\epsilon] , & m = 0 ; \end{cases} \quad (3.11)$$

since only the first absolute moment and the even moments are required in the present calculations. When $a \gg b/2$, a good approximation is

$$|D|_m(\epsilon) \approx C m! a^{1-m} \exp[(1-b)\epsilon]. \quad (3.12)$$

The values of the parameters a , b , C were then derived from these moments, and the steady-state master equation was solved to yield the nonequilibrium correction factor k/k_e .

IV. RESULTS

4.1 The Equilibrium Transition Rate and Energy Transfer Moments

The low-order energy transfer moments calculated using Equation (3.8) are summarized in Table II. Figure 1 shows a plot of $[N(\epsilon)/N_0(\epsilon)]/[1 - \exp(-kT/D)]$ versus ϵ for the system $N_2 + Ar$. Although the scatter in the data are considerable, the empirical form

$$N(\epsilon)/N_0(\epsilon) = C \exp[(1-b)\epsilon] [1 - \exp(-kT/D)] \quad (4.1)$$

where D is the well depth of the interaction potential between the third body and one of the recombining atoms does correlate the data with reasonable accuracy. Thus the parameters C and b were both determined from this figure.

The parameter C is the high-temperature limit of the barrier rate recrossing correction factor $N(0)/N_0(0)$. Recently Keck¹⁴ has suggested a new empirical expression

$$\frac{N(0)}{N_0(0)} = 1 - 0.7 \left[\frac{m_2}{m_1 + m_2} \left(\frac{m_3}{m_1 + m_3} \right)^{1/2} + \frac{m_1}{m_1 + m_2} \left(\frac{m_3}{m_2 + m_3} \right)^{1/2} \right] \quad (4.2)$$

which is able to correlate all the data obtained to date (including highly asymmetric diatomic molecules). The possible temperature dependence of the parameter b was also investigated, but the statistics

were not good enough to give a definite answer, and the average value of b was used in the following calculations. The values of C and b are summarized in Table III.

A possible correlation of the parameter b and the atomic masses of the system is shown in Figure 2 where b is plotted versus $[m_3/(m_1 + m_2)]^{1/2}$. The straight line

$$b = \exp\{-0.25 [m_3/(m_1 + m_2)]^{1/2}\} \quad (4.3)$$

represents the data points quite well. However, results for the systems $H_2 + Ar$ or $H_2 + Xe$ are perhaps needed to verify this correlation since these systems have large values of the factor $[m_3/(m_1 + m_2)]^{1/2}$ (4.47 and 8.09, respectively). The data plotted in Figure 2 include the systems $HCl + Ar$, $N_2 + Ar$, $Cl_2 + Ar$, $O_2 + Xe$, $O_2 + Ar$, and $I_2 + Ar$.¹⁵

The parameter a was obtained by taking the average of the four values of $2|D|_1/D_2$ in Table II and using the relationship

$$2|D|_1/D_2 = \alpha\beta \quad (4.4)$$

which follows from Equation (3.11). The values of a for all the cases studied are summarized in Table III and plotted versus kT/D in Figure 3, where D is the well depth of the interaction potential for the recombining molecule. A weak temperature dependence of a is definitely observed in Figure 3, but the data are insufficient to determine any mass dependence. The line of best least-squares fit (solid straight line in the figure) shows scatters within the statistical errors. Consequently, for the data obtained to date, the parameter a can be reasonably well estimated from the formula

$$a = 3.47 (kT/D)^{0.232} . \quad (4.5)$$

The average energy transfers involved in reactive collisions of three-body recombination and dissociation processes are also of interest and can be evaluated directly from the moments summarized in Table II. The averaged absolute energy transfer per collision, $\langle \Delta \rangle$, and the root-mean-square energy transfer per collision, $\langle \Delta^2 \rangle^{1/2}$, are plotted in Figure 4 versus kT/D where D is the well depth of the interaction potential of the molecule. The best least-squares-fit lines (solid lines in the figure) correlate the data reasonably well and can be represented by the following equations.

$$\begin{aligned}\langle \Delta \rangle &= 0.10 (kT/D)^{-0.30} \\ \langle \Delta^2 \rangle^{1/2} &= 0.22 (kT/D)^{-0.28}\end{aligned}\quad (4.6)$$

Tables IVa, IVb, and IVc show the distributions of the trajectories classified according to the nature of their end states (see Reference 8). The cases shown are

- (a) $N_2 + Ar$ at $11500^\circ K$ ($kT/D = 0.1$), $\epsilon = 0$;
- (b) $N_2 + Ar$ at $100^\circ K$ ($kT/D = 0.0009$), $\epsilon = 0$;
- (c) Same as (b), but with all trajectories that came from a bound $N\cdot Ar$ complex removed.

Although these distributions have similar general features as those obtained by Keck,⁶ one major difference is that the number of trajectories which cross the energy surface more than once in each direction increases as the temperature is lowered. This produced a temperature dependence of the recrossing factor N/N_0 although the total number of $f \rightarrow b$ trajectories did not vary significantly with temperature. This behavior illustrates the effects of the attractive minimum in the third-body interaction potential at low temperatures. It also explains the

reason why Keck⁶ did not observe a similar temperature dependence for N/N_0 (he used purely repulsive third-body interaction potentials).

In order to complete the determination of the transition kernel, $R(\epsilon_i, \epsilon_f)$ and produce a map of its relative numerical distribution, the function $G(\epsilon_f)$ in Equation (3.3) must first be found. The function

$$G(\epsilon) = [1 - (-\epsilon/\delta)^{1/2}]/[1 + (-\epsilon/\delta)^{1/2}] \quad (4.7)$$

where $\delta = D/kT$, was used for $G(\epsilon_f)$ in the present calculations since Keck² found that it was able to represent the numerical calculations of $R_v(\epsilon)/R_v(0)$ with sufficient accuracy. The resulting numerical distributions of $R(\epsilon_i, \epsilon_f)/R_v(0)$ are shown in Figure 5 for $N_2 + Ar$ at 11500°K. The figures in the boxes represent the mean value of $R(\epsilon_i, \epsilon_f)/R_v(0)$ for the box. Because of the sampling technique employed, each value of ϵ used in the calculations yielded data in a quadrant that touches the diagonal $\epsilon_i = \epsilon_f$, at a value of $\bar{\epsilon} \equiv (\epsilon_i + \epsilon_f)/2 = \epsilon$. Data in overlapping quadrants agreed within the statistical errors and were averaged to obtain the results shown. The total number of trajectories sampled was approximately three hundred for each value of ϵ ($\epsilon = 0, -1, -2, -3$). The results shown were calculated for $\epsilon_i > \epsilon_f$ (recombination); however, since $R(\epsilon_i, \epsilon_f)$ is symmetrical in ϵ_i and ϵ_f , the values for $\epsilon_i < \epsilon_f$ may be obtained by reflection in the diagonal $\epsilon_i = \epsilon_f$. The maps show that $R(\epsilon_i, \epsilon_f)$ exhibits a sharp maximum ridge along $\epsilon_i = \epsilon_f$, which corresponds to zero energy transfer; this dies off rapidly as $|\epsilon_i - \epsilon_f|$ increases. Substitution of Equation (3.10) into Equation (3.3) yields

$$R(\epsilon_i, \epsilon_f)/R_v(0) = Ca\beta G(\epsilon_f) \exp(\alpha\epsilon_f - \beta\epsilon_i). \quad (4.8)$$

Since the parameters α, β are simply related to the parameters a, b by Equation (3.4), Equation (4.8) could be used to generate the function

$R(\epsilon_i, \epsilon_f)/R_v(0)$. The results are plotted in the upper left corner of Figure 5 as a contour map. It can be seen that the contour map reproduces all the important features of the corresponding actual distribution, and the agreement in general is very good.

Figure 6 shows a plot of $[R(\Delta, \bar{\epsilon})/R_v(0)]/[R(\epsilon)/R(0)]$ versus Δ . The factor $[R(\epsilon)/R(0)]$ was included for normalization purposes so that the data could be better represented by a single line. In the plot, the solid line passing through the bulk of the data points has a slope equal to the parameter a as determined above (see Table III). It can be seen that for $\Delta < 0.5$, the data points deviate considerably from this line; however, the region around $\Delta \approx 1$ has the most important contribution in the determination of the nonequilibrium correction factor, and the line fits the data very well in this region.

It can therefore be concluded that the functional form for $R(\epsilon_i, \epsilon_f)$ and the associated parameters determined above (Equation (3.3) and Table III) lead to a very good representation of the transition kernel. At the same time, it is still simple enough so that the steady-state master equation can be solved analytically without the usual reliance on a great deal of numerical computation.

The nonequilibrium correction factors were then calculated as was done in Reference 8.

4.2 Recombination and Dissociation Rate Coefficients

(1) The "Chaperon" Mechanism

One of the consequences of including an attractive well in the third-body interaction potential is that it provides a "chaperon" mechanism (or "complex" mechanism) in which long-lived X·N complexes

serve as an intermediate species in the reaction process, in addition to the usual "energy transfer" mechanism. Since the trajectory calculations provide complete histories of the collisions, those trajectories which contained a bound complex pair at the beginning ($t \rightarrow -\infty$) of the collision could be identified by calculating the relative energies of the X·M and Y·M pairs. The results are shown in Figure 7 as a plot of N_C/N_{NC} versus kT/D_{X^1} , where N_C/N_{NC} is the ratio of the effective number of reactive trajectories from the complex mechanism to that from the non-complex mechanism, and D_{X^1} is the well depth of the third-body interaction potential (see Table I). The data plotted include results for the systems $N_2(X^1\Sigma_g^+)$ + Ar, $N_2(A^3\Sigma_u^+)$ + Ar, and $Cl_2(X^1\Sigma_g^+)$ + Ar and can be represented very well by the line

$$N_C/N_{NC} = 0.74 (kT/D_{X^1})^{-3/2} . \quad (4.9)$$

The complete recombination process can now be represented by the following reactions:



The usual rate law is

$$\begin{aligned} d[X_2]/dt &= -d[X]/2dt \\ &= k_3[X][X \cdot M] + k_5[X]^2 [M] , \end{aligned} \quad (4.11)$$

and

$$N_C/N_{NC} = k_3[X \cdot M]/k_5[X][M] . \quad (4.12)$$

Since reactions (4.10a) in general proceed at much higher rates than reactions (4.10b) and (4.10c), local thermodynamic equilibrium may be assumed to exist between X, M, and X·M. Thus

$$[X][M]/[X \cdot M] = K_e = k_2/k_1 \quad (4.13)$$

where K_e is the corresponding equilibrium constant.

It follows that

$$N_C/N_{NC} = k_3/(K_e k_5) . \quad (4.14)$$

The classical phase integrals required for the determination of K_e were evaluated numerically for a Morse oscillator using the parameters listed in Table III. The results show that within the temperature range considered ($0.5 < kT/D_{XM} < 5$) ,

$$K_e = C(kT/D_{XM})^{3/2} \quad (4.15)$$

to a very good approximation, where C is a constant. Hence, from Equations (4.9) and (4.14), the ratio k_3/k_5 must be nearly independent of the temperature within the temperature range considered.

The problem of the "complex" mechanism and the "energy transfer" mechanism has been studied by a number of investigators,¹⁶⁻²² and the equilibrium constant (Equation 4.13) has also been calculated in other studies.²³⁻²⁶ For the purpose of comparing with all the available experimental measurements, however, the results are still very inconclusive.

The creation of the "complex" mechanism is, of course, by no means the only effect of the attractive minimum in the third-body interaction potential. Apart from the bound complexes ($H - B < 0$), which include both the truly bound ($H < 0$) and the quantum mechanically metastable

($0 < H < B$) complexes, one can define the quasidimers ($B < H < B_m$) as was done by Kim and Ross.²⁶ "Energy transfer" can take place both during the repulsive and attractive phases of the collisions. In addition, the attractive minimum in the $X + M$ interaction enhances reaction rates by increasing the density of representative points in the reaction region of the phase space (see Reference 5 for a discussion on this topic for the $H + H + H_2$ recombination). These contributions are all included in the classical phase-space theory of reaction rates developed by Keck and his coworkers.

The recent work of Clarke and Burns²⁷ shows some interesting features of the "complex" mechanism of the recombination of bromine. However, their comparisons and conclusions are meaningful only when the overall recombination rate is dominated by the complex mechanism. The work of Keck and his coworkers¹⁻⁵ and the present results clearly show that this condition is satisfied only when $kT \lesssim D_{XM}$. At higher temperatures the energy transfer mechanism becomes more and more important, and the overall reaction cannot be represented by the complex mechanism alone.

(2) Barrier Penetration

Classically, the barrier surface provides an unambiguous dividing surface in phase space which separates the reactants ($X + Y + M$) from the products ($XY + M$) of the reactions under consideration. Quantum mechanically, however, this surface has "holes" due to barrier penetration; i.e., some reactants can react and form products without passing through the barrier surface.

The effect of barrier penetration on reaction rates is twofold.

First, it increases the barrier rate coefficient k_r^B by an amount equal to the effective recombination rate due to barrier penetration. Second, it may change the steady-state distribution of the population of energy states by supplying extra molecules to states near the barrier surface, resulting in a change of the nonequilibrium correction factor (k/k_e). These effects must be evaluated by solving a new set of master equations which include barrier penetration as additional source terms. This completely destroys the simplicity shown in Section III and Reference 8 where the steady-state master equation was solved analytically for a separable kernel. Fortunately, for most practical potential energy barriers (in particular, the one used here), the transmission coefficient (probability of barrier penetration) at an energy ϵ decays extremely rapidly as ϵ varies from 0 to $-B/kT$. Thus a new energy surface ($\epsilon = \epsilon_b$) may be defined, such that the recombination rate due to barrier penetration at energy levels below ϵ_b is negligible compared with the recombination rate due to collisional deactivation through the energy surface $\epsilon = \epsilon_b$. Using this surface as the new boundary (instead of $\epsilon = 0$) and solving the steady-state master equation in a manner similar to that of Reference 8, the factor

$$[\mathcal{R}(\epsilon_b)/\mathcal{R}(0)][(k/k_e)_{\epsilon=\epsilon_b}/(k/k_e)_{\epsilon=0}] \approx \exp(-b\epsilon_b) \quad (4.16)$$

was obtained which must multiply the factor k/k_e in Equation (1.1) to include effects of barrier penetration.

In order to determine ϵ_b , an effective recombination rate coefficient due to barrier penetration is defined as

$$k_p(\epsilon_b) \equiv Q_p(\epsilon_b) [X]^{-2} [M]^{-1} \quad (4.17)$$

where $Q_p(\epsilon_b)$ is the total barrier penetration rate for $\epsilon < \epsilon_b$ and is given by

$$Q_p(\epsilon_b) [X]^{-2} = 2\sigma(8kT/\pi\mu)^{1/2} \int_{-B/kT}^{\epsilon_b} T_r(\epsilon) \exp(-\epsilon) d\epsilon. \quad (4.18)$$

Here σ is a collision cross-section, and $T_r(\epsilon)$ is the transmission coefficient calculated using the semi-classical equation

$$T_r(\epsilon) = \exp[-(2/h) \int_{x_1}^{x_2} \{2\mu[V(x)/kT - \epsilon]\}^{1/2} dx] \quad (4.19)$$

where h is the Planck's constant, $V(x)$ is the potential energy, and x_1 and x_2 are the two positions at which $V/kT = \epsilon$. Equations (4.18) and (4.19) were then integrated numerically. The results for nitrogen are shown in Figure 8 where k_p is plotted versus ϵ_b , from which the new surface $\epsilon = \epsilon_b$ can be approximately located with the condition

$$k_p(\epsilon_b) = k_r^B(N/N_0). \quad (4.20)$$

For example, for nitrogen at 100 °K, $k_r^B(N/N_0) \approx 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$ which gives $\epsilon_b \approx -0.35$, and from Equation (4.16) the corresponding increase in rate due to barrier penetration is a factor of 1.3 approximately. It should be pointed out that because k_p varies rapidly with ϵ_b , the determination of ϵ_b is very insensitive to slight variations in σ , $[M]$, and $k_r^B(N/N_0)$. Therefore, high accuracy is not required in estimating these quantities.

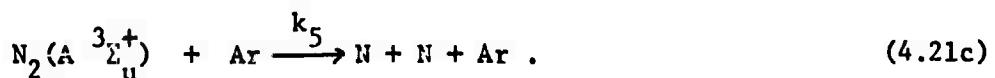
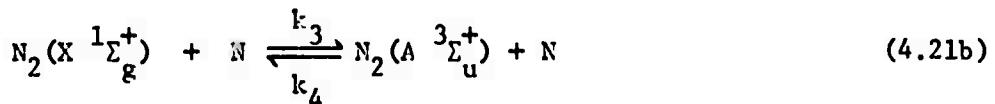
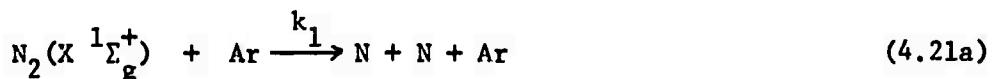
(3) Corrections Due to Deviations of the Morse Form from True Potentials

The Morse form (Equation (2.2) and Table I) used to represent the interaction potential V_{N_2} was found to deviate considerably, in the long-range asymptotic region, from the more accurate potential curves

given by Gilmore.²⁸ A plot of Gilmore's potentials versus the separation shows that the form $C_6 r^{-6}$ is a much better representation of the true potentials in this region ($r \gtrsim 1.5 \text{ \AA}$). The major effect of incorporating this modification is that it alters somewhat the position of the rotational maximum z_2 and thereby changes the barrier rate coefficient (Equation (2.9) of Reference 3) through the factor $z_2^2(z_2 - z_1)$. Denoting the new barrier rate coefficient by k_6^B , the ratio k_6^B/k_r^B is included in Table V. The corrections are fairly small, but they do introduce an additional weak negative temperature dependence.

(4) Contribution from the $A^3\Sigma_u^+$ State

The overall dissociation process for nitrogen may be described satisfactorily by the following set of reactions:



It has been pointed out previously (see Reference 3 and references quoted there) that the $A^3\Sigma_u^+$ state makes significant contributions to the overall reaction rates. In order to properly account for these contributions, the concentration $[N_2(A^3\Sigma_u^+)]$ must be found. A steady-state analysis yields

$$[N_2(A^3\Sigma_u^+)]_s / [N_2(A^3\Sigma_u^+)]_e = \{1 + (k_5/k_4)[Ar]/[N]\}^{-1} \quad (4.22)$$

where the subscript s denotes steady-state, and e denotes local equilibrium. Since the ratio k_5/k_4 was not known, the previous calculations^{3,4}

simply assumed that the A $^3\Sigma_u^+$ state was in local thermal equilibrium with the ground state. Recently Flagan and Appleton²⁹ have obtained the expression

$$k_4 = 5.1 \times 10^{-3} T^{-2.23} \text{ cm}^3 \text{ sec}^{-1} \quad (4.23)$$

for $6000^\circ \text{ K} \lesssim T \lesssim 14000^\circ \text{ K}$, by matching the computed peak intensity of the nitrogen first-positive radiation with Wray's experimental measurements.³⁰ The result of the steady-state analysis, Equation (4.22), may therefore be used in calculating the rate coefficients. A plot of the ratio $[N_2(A ^3\Sigma_u^+)]_s / [N_2(A ^3\Sigma_u^+)]_e$ as a function of the temperature shows that the assumption of local thermodynamic equilibrium between the A-state and the ground state is valid for temperatures $< 4000^\circ \text{ K}$ (which covers all recombination rate measurements), but the contribution from the A-state decreases rapidly at higher temperatures.

Taking into account effects of barrier penetration and corrections due to deviations of the Morse form from true interaction potentials for nitrogen, the results of the calculated recombination rate coefficients are summarized in Table V and plotted in Figure 9 as a function of the temperature. The theoretical points $\blacklozenge [(k_r(X ^1\Sigma_g^+) + k_r(A ^3\Sigma_u^+))]$ and $\bullet [k_r(X ^1\Sigma_g^+)]$ have been connected visually by full lines to help in comparing the results. The dashed line represents the theoretical predictions of $k_r(X ^1\Sigma_g^+)$ without the corrections due to barrier penetration and deviations of V_{N_2} from the Morse form. It is seen from the figure that at low temperatures, the present theoretical predictions of the recombination rate coefficient, $[k_r(X ^1\Sigma_g^+) + k_r(A ^3\Sigma_u^+)]$, are in very good agreement with the experimental

measurements of Campbell and Thrush³¹ (Δ), and Clyne and Stedman³² (\circ); the more recent room temperature measurement of Brennen and Shane³³ (∇) is somewhat higher but also appears to be within the combined statistical errors. There still exists a discrepancy of about a factor of 6 between Clyne and Stedman's measurement at 90 °K and the theoretical prediction at 100 °K. However, since Clyne and Stedman used pure nitrogen in their experiment, the different efficiencies of N_2 and Ar as third bodies may be responsible for this discrepancy. In this regard, experimental measurements at $T \approx 100$ °K using Ar as the third body should be very useful.

For the purpose of effecting a comparison, the experimental dissociation rate measurements have been converted into equivalent recombination rate coefficients through the equilibrium constant. The results of Appleton, Steinberg, and Liquornick³⁴ (A) are in excellent agreement with the theoretical predictions. The results of Byron³⁵ (B) and Cary³⁶ (C) appear to be somewhat higher, but in view of the extent of experimental error and the uncertainties in the theory, the agreement is considered to be very good.

V. DISCUSSION

A number of trajectories for the collision of $N_2 + Ar$ are shown in Figure 10 where two different coordinate systems have been used in order to show certain special features of the collisions more satisfactorily. One coordinate system has the argon atom stationary, with the two nitrogen atoms moving about and is particularly useful for illustrating the individual collisions between each nitrogen atom and the argon atom.

The other coordinate system has the center of mass of the nitrogen molecule stationary with all three atoms in motion. This system offers a good visualization of the internal relative motion of the bound nitrogen molecule. A bound NAr complex is clearly illustrated in Figure 10(c).

It should be pointed out that for convenience of representation in two dimensions, the trajectories shown in Figure 10 have all three particles moving in the same plane. However, the calculations were, in general, three dimensional.

Typical reactive trajectories for $N_2 + Ar$ collisions may be divided into the following types:

(i) Simple $f \rightarrow b$ Trajectories

The three atoms start as free particles and approach close enough for energy and momentum exchanges of appreciable amount to occur. One of the nitrogen atoms transfers sufficient energy to the argon atom. The latter moves away from the bound nitrogen molecule with increased kinetic energy, as in Figure 10(a).

(ii) Trajectories Involving Complexes

As shown in Figure 10(c), one nitrogen atom is initially bound to the argon atom by the weak attractive forces, forming an NAr complex. Another nitrogen atom approaches the complex, and its strong attractive valence forces acting on the first nitrogen atom pulls the latter away from the argon atom, resulting in a reactive trajectory.

(iii) Trajectories with Multiple Crossings of the Barrier Surface

A high temperature trajectory of this type is shown in Figure 10(b) in which the argon atom exchanges energy and momentum with each of the two nitrogen atoms, resulting in the reactive transition ($b \rightarrow f \rightarrow b$).

At low temperatures, however, the attractive minimum in the NAr interaction potential becomes important, and a single nitrogen atom may exchange energy and momentum to and from the argon atom more than once during a collision, resulting in a trajectory with multiple crossings of the barrier surface.

Figures 11(a) and (b) show the time evolution of some of the trajectories examined above. The upper half of these figures plots the energy of the molecule $[(H - B)/kT]$ versus the time ($v_e t$, where v_e is the ground state vibrational frequency of the molecule), and the lower half shows the quantities r_{XY} and r_3 as functions of time. It can be seen that the molecular vibrations are highly anharmonic, and the energy exchanges are typically of order kT or less (see also Figure 12).

For a collision to be reactive (consider recombination), the molecule must start in a free state and end in a bound state. The corresponding energy changes must be such that $H - B < 0$, where H is the Hamiltonian of the molecule, and B is the height of the rotational barrier. Figure 12 shows a distribution plot of ΔH and ΔB for the reactive trajectories of the case $N_2 + Ar$ at $11500^{\circ}K$ on the surface $\epsilon = 0$. In Reference 8, it was shown that for $HCl + Ar$, recombination (the change from $H - B > 0$ to $H - B < 0$) is achieved by two equally

important mechanisms, i.e., reducing H and/or increasing B. For $N_2 + Ar$, on the other hand (see Figure 12), most recombinations are achieved by reducing H. This furnishes further evidence that rotational energy transfer in highly asymmetric molecules plays a relatively important part in chemical reactions.

The distributions of the energy of the recombined nitrogen molecules are shown in Figure 13 for several temperatures, where E_{XY} is the total energy of the molecule, B_{XY} is the height of the rotational barrier (see Reference 2), and $(E - E)_{XY}$ is a measure of the vibrational energy of the molecule. Figure 14 shows plots of the distribution of trajectories with respect to the impact parameter (b_M) and the kinetic energy (E_M/kT), respectively, of the argon atom relative to the center of mass of the nitrogen molecule. The reactive trajectories are indicated by the shaded area in these figures.

For trajectories which involve bound $N\cdot Ar$ complexes, we define the impact parameter (b_c) and the kinetic energy (E_c/kT) of the free nitrogen atom relative to the center of mass of the $N\cdot Ar$ complex. The distributions with respect to these two parameters are plotted in Figure 15 (for $T = 100^{\circ}K$). Again, the reactive (recombination) trajectories are indicated by the shaded area.

It is interesting to note the characteristics of the impact parameter distributions. The number of trajectories (N) approaches zero for $(b_M, b_C) \rightarrow 0$. This is a geometrical effect. As (b_M, b_C) increases, N rises to a maximum and then dies off gradually when the interaction between the argon atom and the nitrogen molecule becomes weaker and weaker.

The results of the Monte Carlo trajectory calculations presented above indicate that the equilibrium transition rate for systems of diatomic molecules highly diluted in an inert gas heat bath can be represented satisfactorily by a simple, separable function which contains three characteristic parameters. It appears that these parameters can be correlated and predicted by the formulas obtained in this study although better statistics and additional data for other systems are probably needed for certain refinements in these formulas. Also, in order to understand more about the effects of the "complex" mechanism to the overall recombination rate coefficient at low temperatures, a detailed analysis of the corresponding master equations (with the appropriate transition rates) must be carried out. Finally, it is of great interest to modify the present Monte Carlo techniques for use with three-body interaction potentials of a more general nature: in particular, for systems that involve strongly reacting third bodies, e.g., H + H + H.

VI. ACKNOWLEDGMENT

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TABLE I

Morse Potential Parameters

System	D(eV)	β (Å $^{-1}$)	r _e (Å)
N ₂	9.90	2.66	1.10
N ₂ (A $^3\Sigma^+$ _u)	3.68	2.70	1.29
NAr	0.017	1.49	3.18

TABLE II

Summary of Energy Transfer Moments

System*	T ^o K (kT/D)	ϵ	$ D _1$	D ₀	D ₂	D ₄	$\frac{D_0}{ D _1}$	$\frac{2 D _1}{D_2}$	$(\frac{12D_2}{D_4})^{1/2}$
$N_2(X)$	11500 (0.1)	0	.366	1.56	.342	2.14	4.26	2.14	1.39
		-1	.373	.876	.391	2.30	2.34	1.91	1.43
		-2	.344	.992	.381	2.74	2.83	1.81	1.30
		-3	.222	.744	.221	.824	3.35	2.01	1.80
		mean					3.21	1.97	1.48
$N_2(X)$	1000 (.0087)	0	.501	1.52	.927	17.4	3.04	1.08	.80
		-1	.395	.600	.988	47.5	1.52	.80	.50
		-2	.280	.479	.587	13.9	1.71	.955	.71
		-3	.309	.456	.540	12.4	1.48	1.14	.72
		mean					1.94	.99	.68
$N_2(X)$	200 (.0017)	0	.332	.481	.817	47.1	1.45	.813	.46
		-1	.229	.234	.732	100.	1.02	.626	.29
		-2	.191	.353	.471	14.6	1.85	.811	.62
		-3	.147	.144	.338	6.24	.98	.870	.81
		mean					1.32	.78	.54
$N_2(X)$	100 (.0009)	0	.183	.205	.454	11.6	1.12	.807	.69
		-1	.128	.067	.503	40.2	.524	.509	.39
		-2	.102	.053	.438	26.8	.520	.466	.44
		-3	.088	.067	.281	16.2	.762	.627	.46
		mean					.73	.60	.50

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TABLE II

Summary of Energy Transfer Moments
(Continued)

System *	T °K (kT/D)	ε	D ₁	D ₀	D ₂	D ₄	D ₀ D ₁	2 r ₁ D ₂	($\frac{12D_2}{D_4}$) ^{1/2}
N ₂ (A)	1000 (.0234)	0	.473	2.04	.784	17.5	4.31	1.21	.73
		-1	.381	.682	.658	9.40	1.79	1.16	.92
		-2	.291	.848	.553	10.4	2.91	1.05	.80
		-3	.233	.606	.387	3.21	2.60	1.20	1.20
		mean					2.90	1.16	.91
N ₂ (A)	200 (.0047)	0	.360	.782	.792	32.4	2.17	0.91	0.54
		-1	.291	.314	.886	96.2	1.08	0.66	0.33
		-2	.201	.256	.548	19.9	1.27	0.73	0.57
		-3	.173	.162	.415	17.9	0.94	0.83	0.53
		mean					1.36	0.78	0.49
N ₂ (A)	100 (.0023)	0	.217	.223	.694	38.8	1.03	.626	.464
		-1	.158	.092	.504	18.7	.582	.628	.569
		-2	.186	.244	.524	19.0	1.31	.748	.576
		-3	.164	.099	.580	34.8	.604	.566	.448
		mean					.882	.642	.514

*The third body is argon.

TABLE III

Summary of Characteristic Parameters
for the Transition Kernel

System*	T °K	kT/D	c	b	$2 D _1/D_2$	a	$1-(\alpha/\beta)^2$
N ₂ (X)	11500	.10	.42	.77	1.97	2.04	.54
	1000	.009	.44	.77	0.99	1.12	.76
	200	.002	.32	.77	0.78	0.94	.83
	100	.001	.25	.77	0.60	0.79	.88
N ₂ (A)	1000	.023	.48	.77	1.16	1.27	.72
	200	.005	.36	.77	0.78	0.94	.83
	100	.002	.24	.77	0.64	0.82	.87

*The third body is argon.

TABLE IV

Distribution of Trajectories with Respect to Class of Reaction and Number of Traverses of the Energy Surface ϵ .

(a) Ar + N₂ at 11500 °K (kT/D = 0.1), ϵ = 0.

Class	n	N			Total
		1	2	3	
(f n b)		103	12	3	118
(f n f)		68	9	1	78
(b n b)		87	3	0	90
(b n f)		10	3	1	14
Total					300

Recrossing correction factor

$$N/N_0 = (103 + 12/2 + 3/3) = 0.37$$

(b) Ar + N₂ at 100 °K (kT/D = 0.0009), ϵ = 0.

Class	n	N					Total
		1	2	3	4	≥ 5	
(f n b)		61	29	9	4	1	104
(f n f)		34	9	3	2	1	49
(b n b)		82	27	6	0	1	116
(b n f)		20	8	1	1	0	30
Total							299

Recrossing correction factor

$$N/N_0 = (61 + 29/2 + 9/3 + 4/4 + 1/5)/299 = 0.27$$

TABLE IV

Distribution of Trajectories with Respect to Class of Reaction and Number of Traverses of the Energy Surface ϵ .
(Continued)

(c) $\text{Ar} + \text{N}_2$ at 100°K ($kT/D = 0.0009$), $\epsilon = 0$,
with non-complex trajectories only.

Class	n	N				Total
		1	2	3	4	
$(f n b)$	30	15	1	1	0	47
$(f n f)$	19	3	2	0	0	24
$(b n b)$	79	24	4	0	1	108
$(b n f)$	19	8	1	1	0	29
Total						208

Recrossing correction factor

$$N/N_0 = (30 + 15/2 + 1/3 + 1/4)/208 = 0.183$$

TABLE V

Recombination Rate Coefficients for N₂ + Ar

State	T °K	$\frac{kT}{D}$	k_r^B	$\frac{N}{N_o}$	$\frac{k}{k_e}$	$\frac{k_6^B}{k_r^B}$	$\frac{\mathcal{R}(\epsilon_b)(k/k_e)\epsilon_b}{\mathcal{R}(0)(k/k_e)_o}$	k_r
X 1Σ ⁺ _g	11500	.1	9.92^{-34}	.42	.22	.60	~ 1	6.14^{-35}
	1000	.009	3.04^{-33}	.44	.60	.77	1.17	7.21^{-34}
	200	.002	9.91^{-33}	.32	.74	1.07	1.26	3.15^{-33}
	100	.001	2.82^{-32}	.25	.82	1.26	1.31	9.49^{-33}
A 3Σ ⁺ _u	1000	.023	6.72^{-33}	.48	.48	.67	1.17	1.20^{-33}
	200	.005	2.32^{-32}	.36	.69	.90	1.26	6.58^{-33}
	100	.002	6.69^{-32}	.24	.77	1.06	1.31	1.70^{-32}

k_r^B and k_r have units cm⁶ molecule⁻² sec⁻¹.

FIGURES

1. Plot of $[N(\epsilon)/N_0(\epsilon)]/[1 - \exp(-kT/D)]$ versus ϵ for $N_2 + Ar$.
●, $T = 11500^\circ K$; ●, $T = 1000^\circ K$; ●, $T = 200^\circ K$; O, $T = 100^\circ K$.
Solid line is the best least-squares fit for all points. The slope of this line determines the parameter b .
2. Correlation of the parameter b with $[m_3/(m_1 + m_2)]^{1/2}$.
3. Correlation of the parameter a with kT/D , where D is the well depth of the interaction potential of the molecule. ▲, $N_2(X^1\Sigma_g^+ + Ar)$; △, $N_2(A^3\Sigma_u^+) + Ar$; ▽, $HCl + Ar$; ▽, $Cl_2 + Ar$; ●, $O_2 + Xe$; O, $O_2 + Ar$; ■, $I_2 + Ar$. Solid line is the best least-squares fit for all points.
4. Plot of the averaged absolute energy transfer, $\langle \Delta \rangle$, and the root-mean-square energy transfer, $\langle \Delta^2 \rangle^{1/2}$, versus kT/D for reactive collisions. D is the well depth of the interaction potential of the molecule. Remainder of legend same as Figure 3.
5. Map of numerical distribution of the function $R(\epsilon_i, \epsilon_f)$ for $N_2 + Ar$ at $11500^\circ K$. The contour map, calculated from Equation (4.8) using the fitted parameters, is plotted in the upper left corner to avoid overcrowding the figure. Comparison may be done by reflection through the diagonal $\epsilon_i = \epsilon_f$.
6. The function $[R(\Delta, \bar{\epsilon})/R_v(0)]/[R(\bar{\epsilon})/R(0)]$ is plotted versus Δ , the absolute value of energy transfer, for the case of $N_2 + Ar$ at $11500^\circ K$. ●, $\bar{\epsilon} = 0$; O, $\bar{\epsilon} = -1$; ▲, $\epsilon = -2$; Δ, $\bar{\epsilon} = -3$. The factor $[R(\bar{\epsilon})/R(0)]$ is included for normalization purposes so that the data can be better represented by a single line. The solid line which passes through the bulk of the data has a slope taken from Table III. See text, Section 4.1.

7. $\frac{k_C}{k_{NC}}$, the ratio of the contribution from the "complex" mechanism to that from the noncomplex mechanism, is plotted versus kT/D_{N_2} , where D_{N_2} is the well depth of the third-body interaction potential.
●, $N_2(X^1\Sigma_g^+)$ + Ar; O, $N_2(A^3\Sigma_u^+)$ + Ar; ▲, Cl_2 + Ar.

8. Plot of the effective recombination rate coefficient due to barrier penetration versus energy, for N_2 at several temperatures.

9. Comparison between theoretical predictions of the recombination rate coefficient and experimental measurements as a function of T.
◆, theoretical predictions of $k_r(X^1\Sigma_g^+)$ + $k_r(A^3\Sigma_u^+)$; ●, theoretical predictions of $k_r(X^1\Sigma_g^+)$; △, Campbell and Thrush³¹; O, Clyne and Stedman;³² ▽, Brennen and Shane;³³ (A), Appleton et al;³⁴ (B), Byron;³⁵ (C), Cary.³⁶ Solid and dashed lines, see text, Section 4.2.

10. Typical trajectories for N_2 + Ar collisions.
(a) Shows f → b transition at 11500°K.
(b) Shows b → f → b transitions at 11500°K. O, position when b → f transition occurred; ●, position when f → b transition occurred.
(c) Shows f → b transition at 100°K. In the upper part, the Ar atom is at the origin; whereas, in the lower part, the origin corresponds to the center of mass of N_2 . The motion of the N·Ar bound complex is clearly illustrated.
The small dots on the trajectories indicate time intervals of $v_e t = 1$ in (a) and (b) and $v_e t = 10$ in (c) where v_e is the ground state vibrational frequency of the molecule.

11. Time evolution of typical trajectories. Upper half of the figure shows energy of the molecule $[(H - B)/kT]$ versus time ($v_e t$). Lower half shows r_{12} and r_3 versus $v_e t$. r_e is the equilibrium separation, and v_e is the ground state vibrational frequency of the molecule.
 - (a) $N_2 + Ar$ at $11500^{\circ}K$,
 - (b) $N_2 + Ar$ at $100^{\circ}K$.
12. Distribution plot of reactive trajectories in the $[\Delta H, \Delta B]$ plane for $N_2 + Ar$ at $11500^{\circ}K$.
13. Energy distributions of nitrogen molecules formed by recombination in argon.
14. Distributions of trajectories (a) with respect to the impact parameter; (b) with respect to the kinetic energy of the third body (see text, Section V) for $N_2 + Ar$ at several temperatures. Reactive trajectories are indicated by the shaded areas.
15. Distributions of trajectories with respect to the impact parameter and the relative kinetic energy defined for the complex mechanism (see text, Section V), for $N \cdot Ar + N$ at $100^{\circ}K$. Reactive (recombination) trajectories are indicated by the shaded areas.

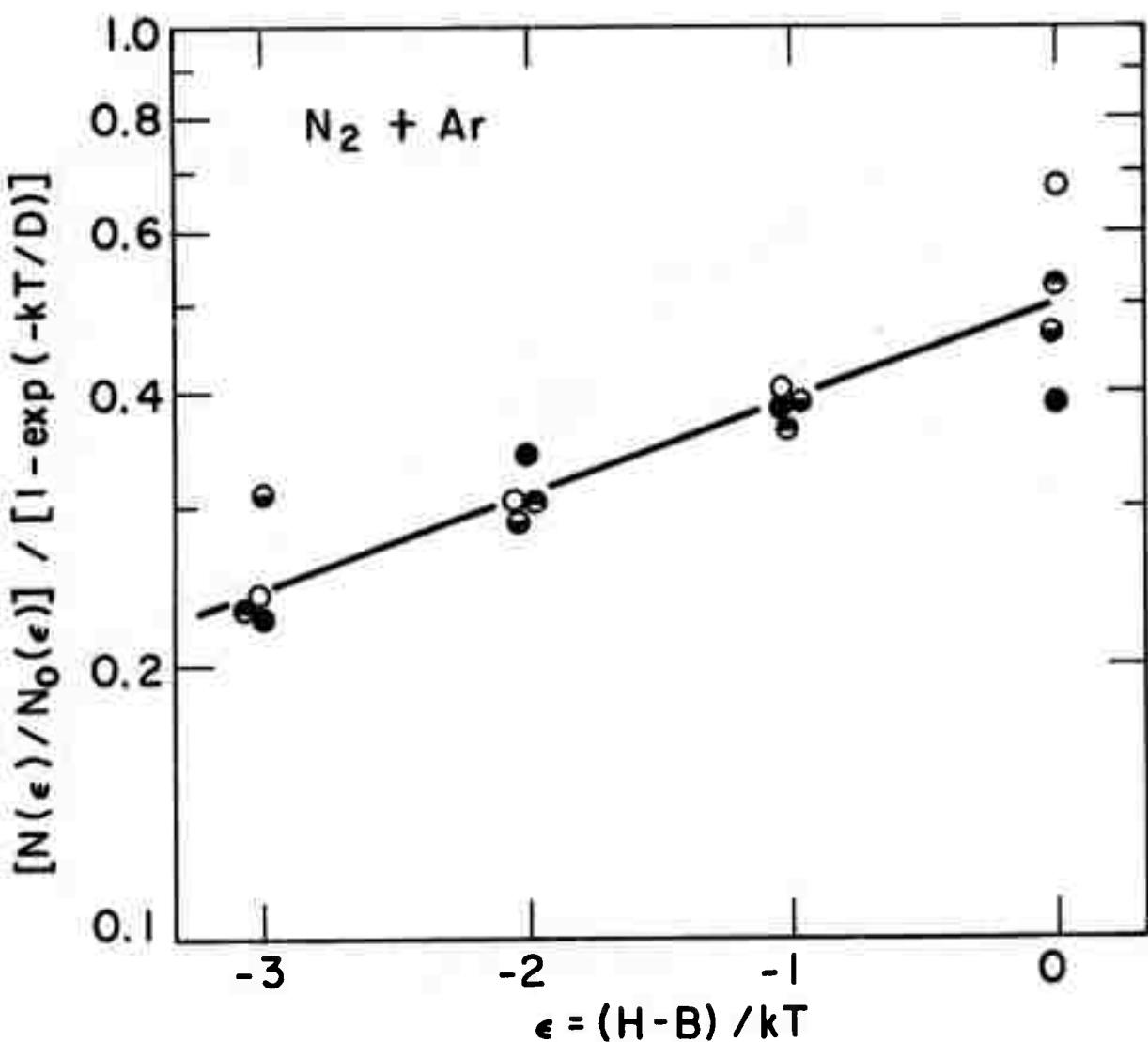


FIG. 1

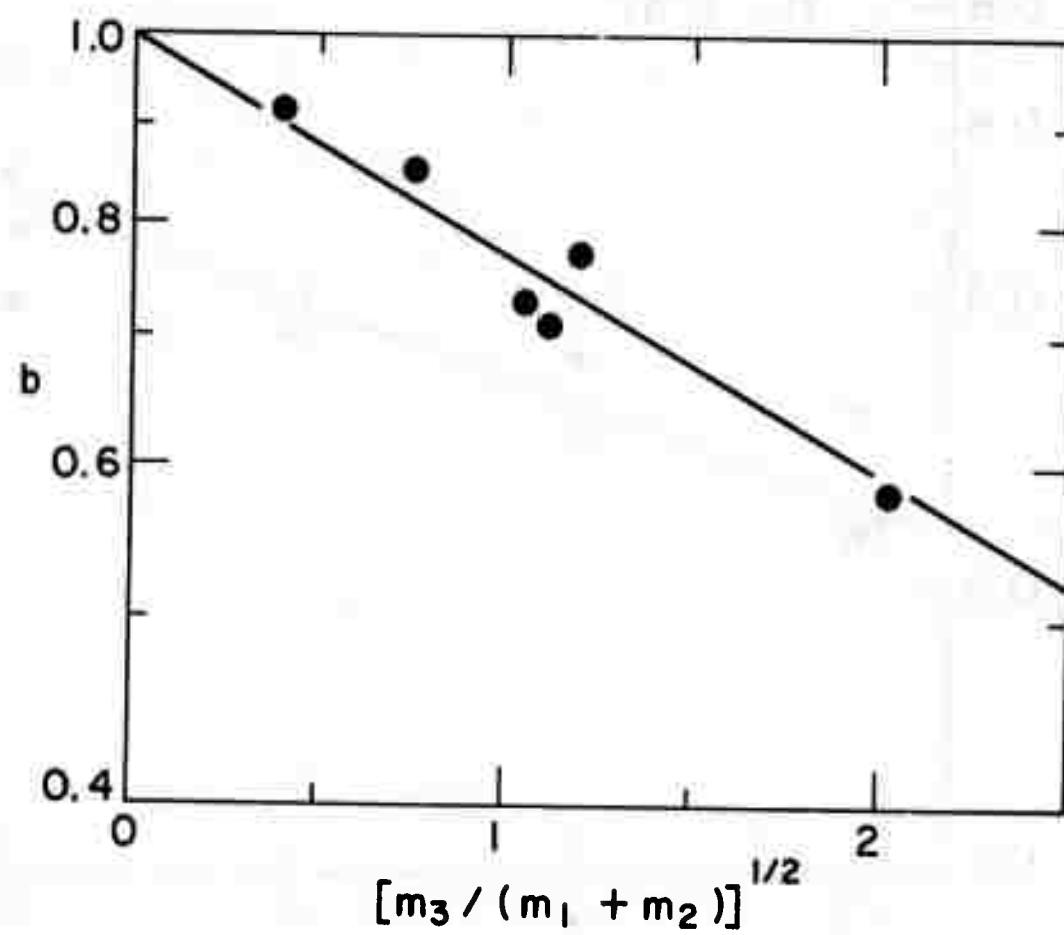


FIG. 2

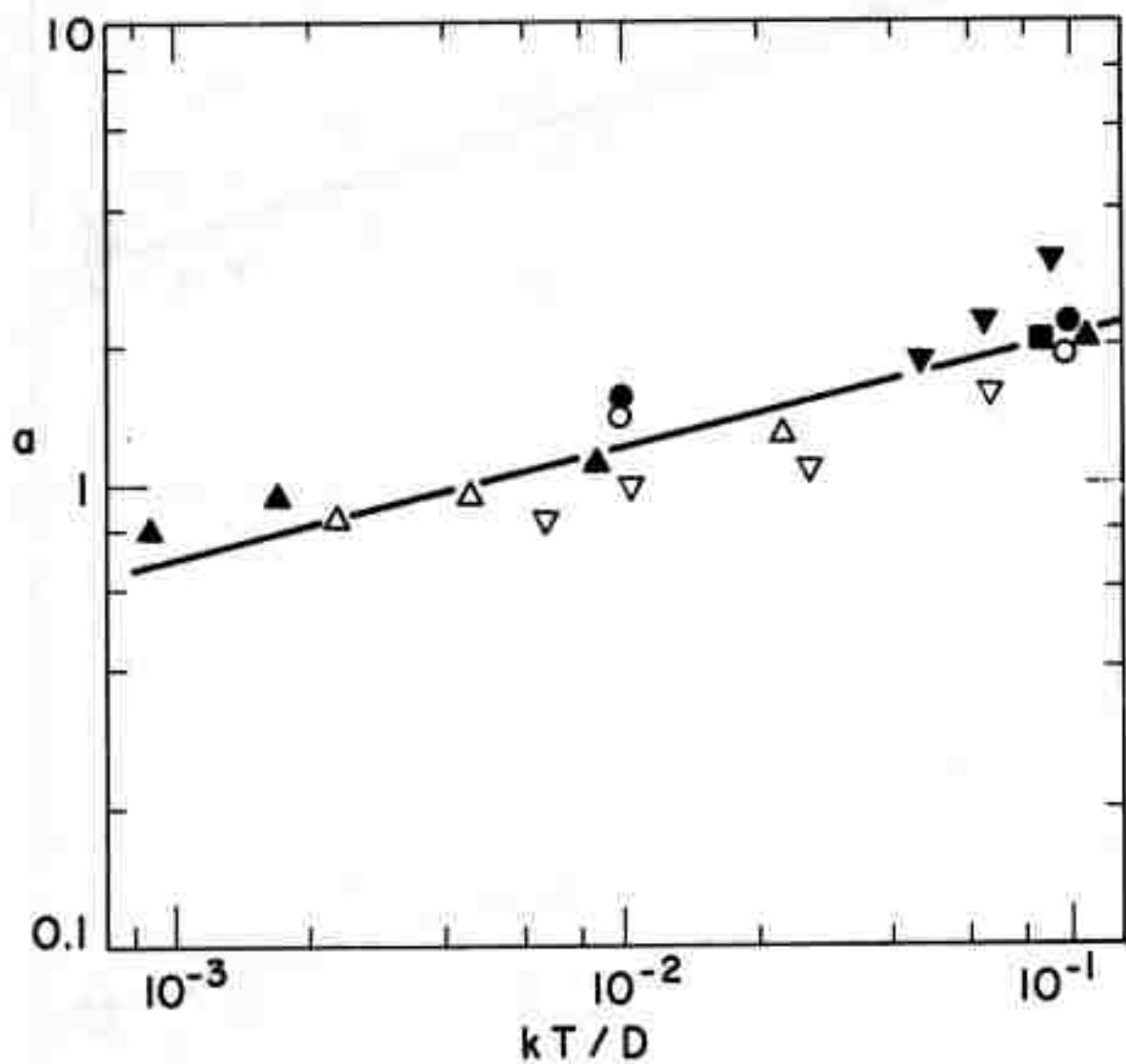


FIG. 3

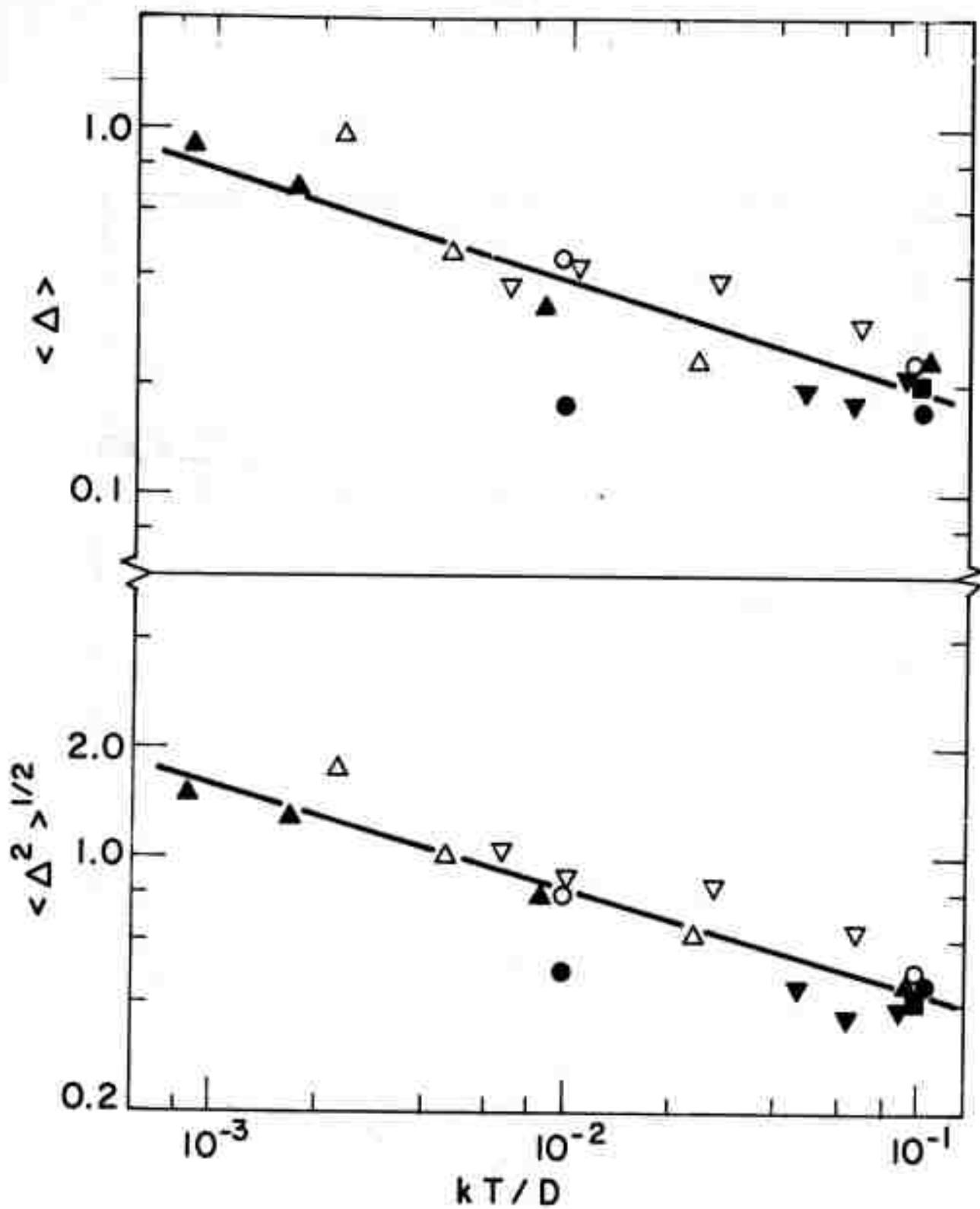


FIG. 4

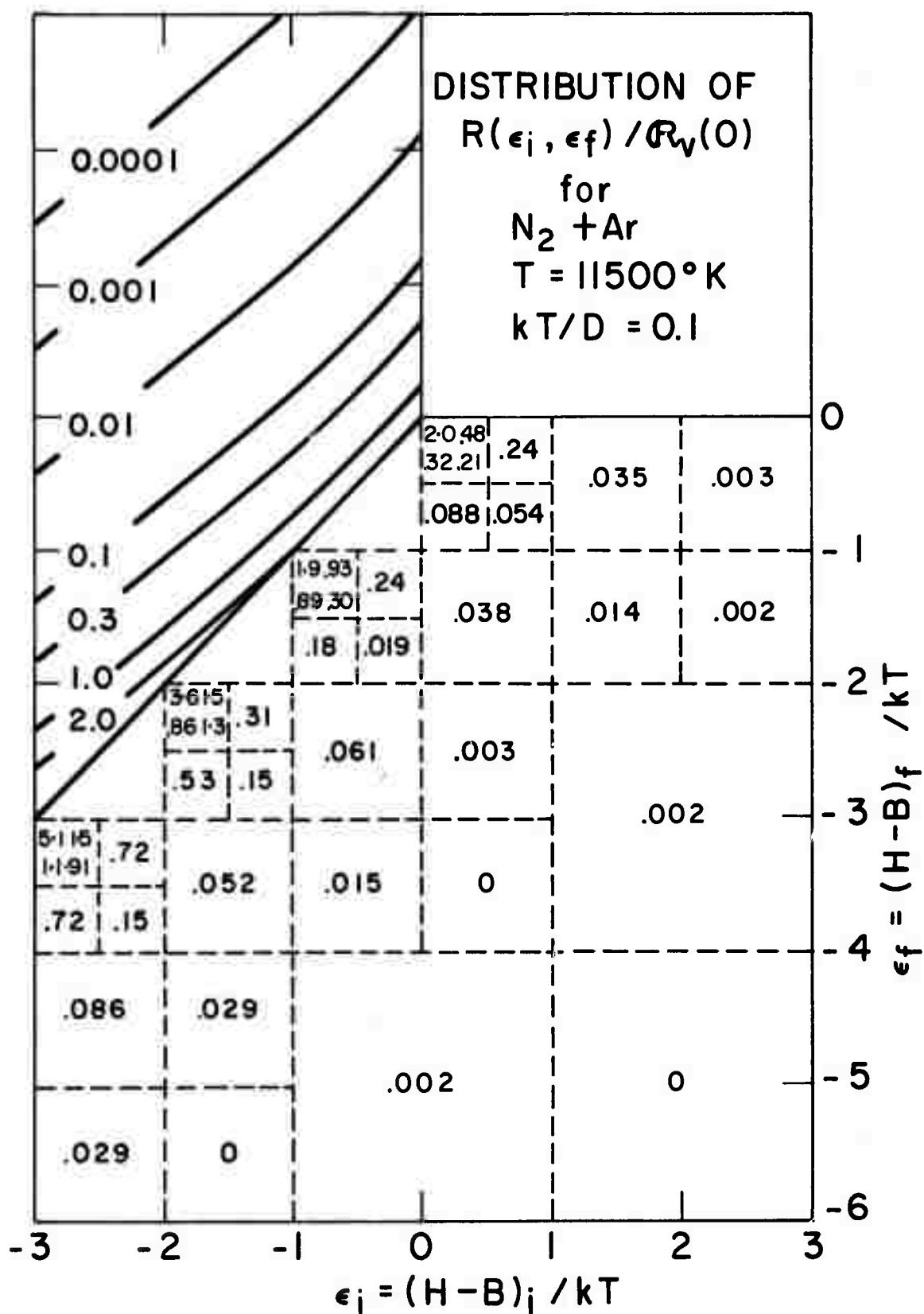


FIG. 5

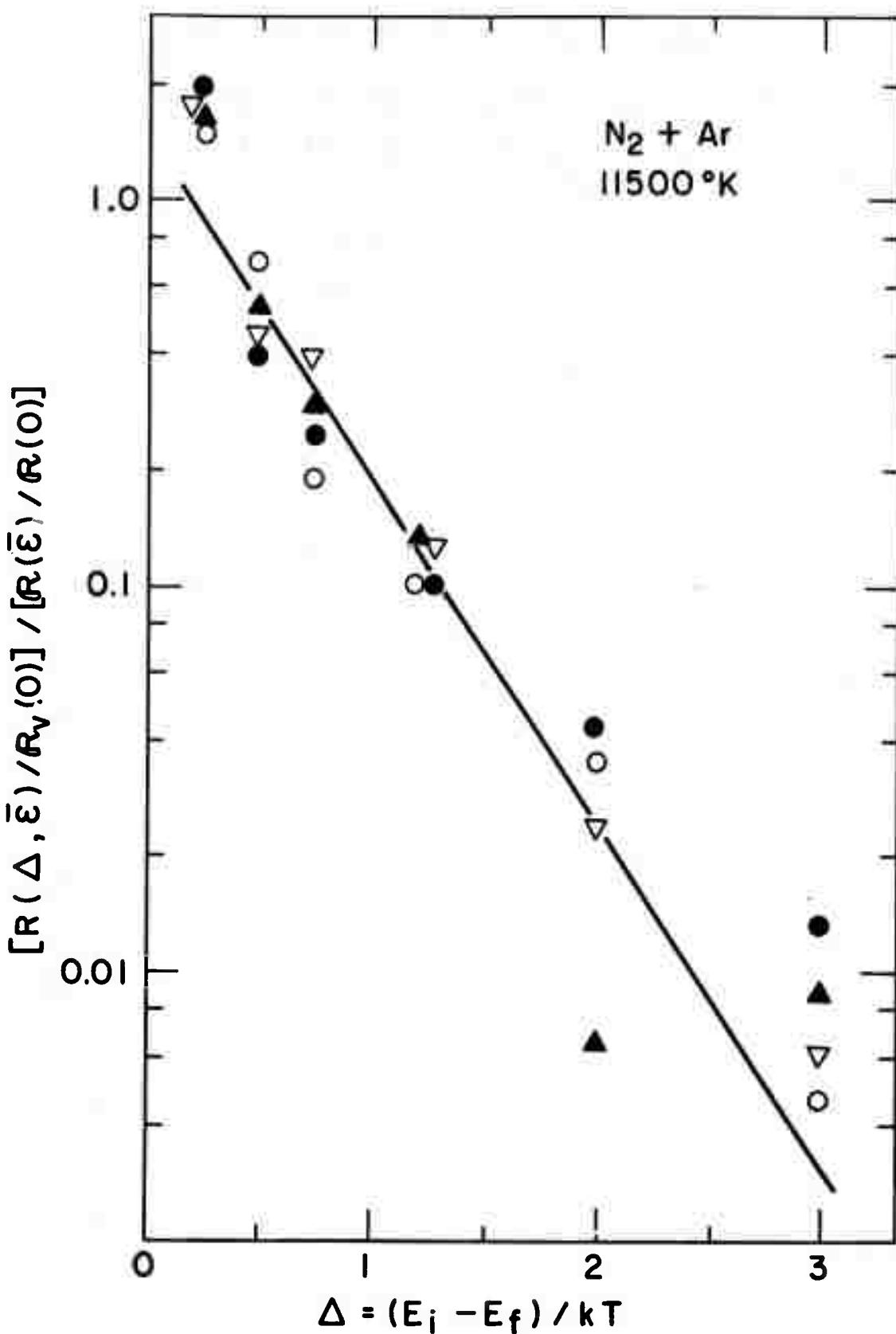


FIG. 6

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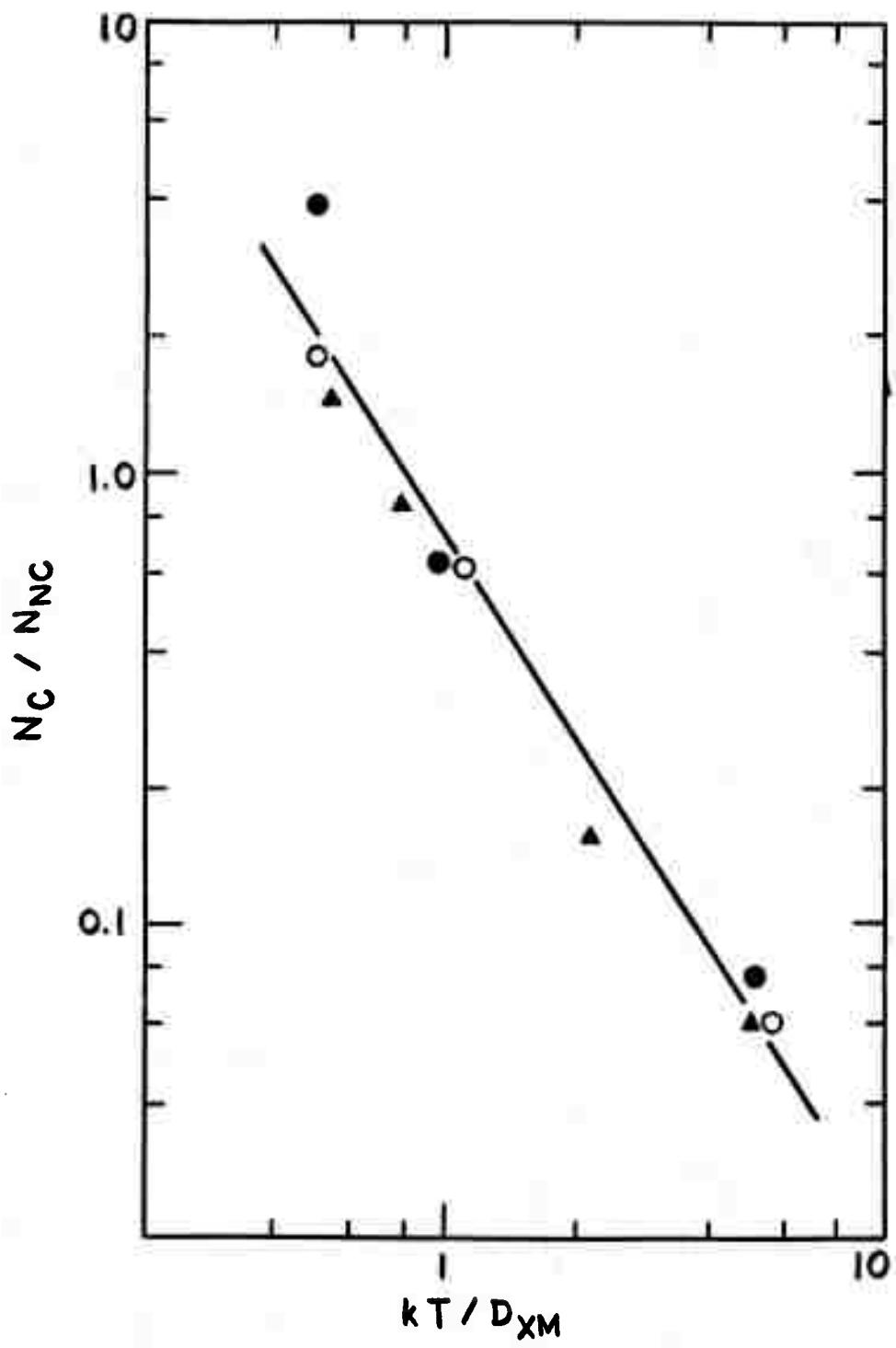


FIG. 7

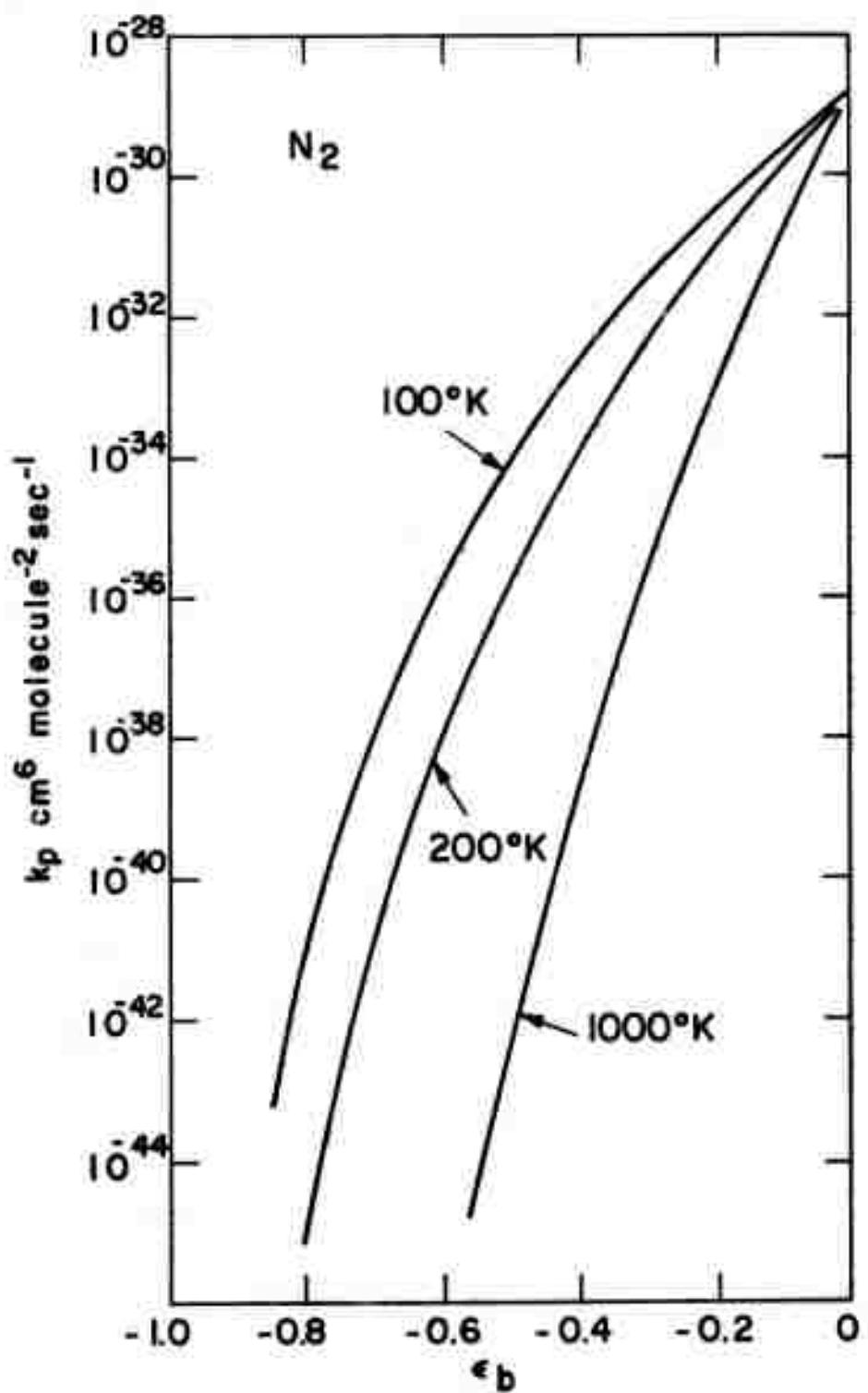


FIG. 8

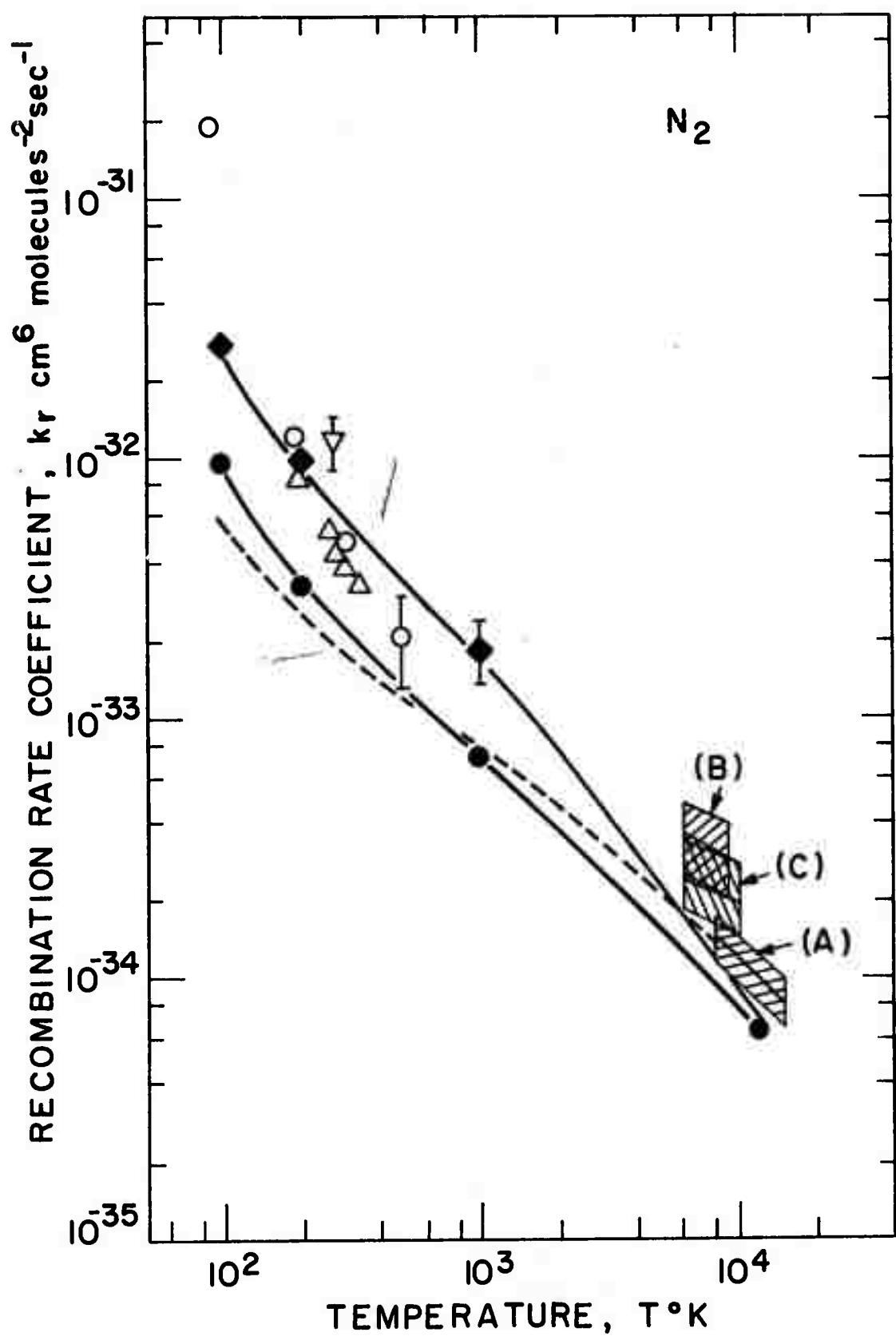


FIG. 3

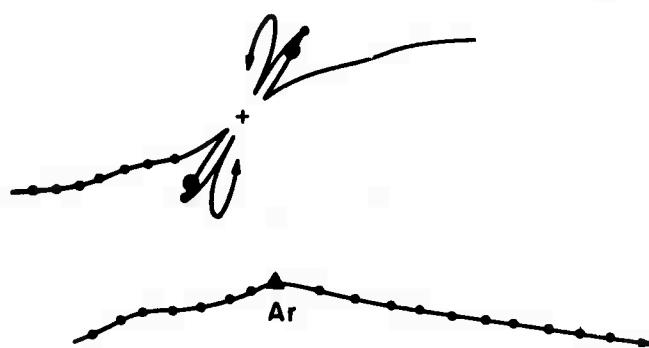
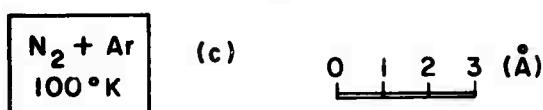
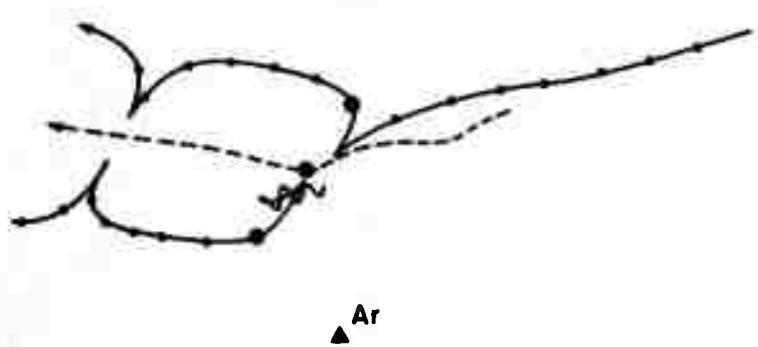
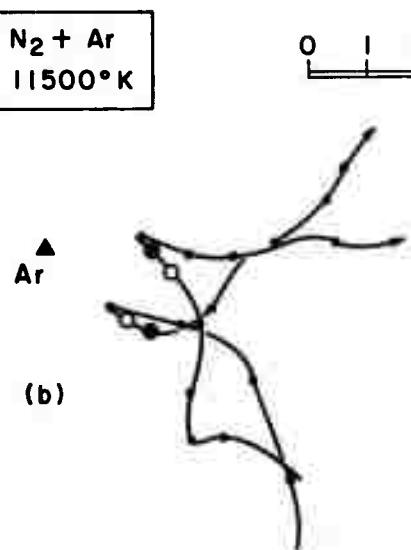
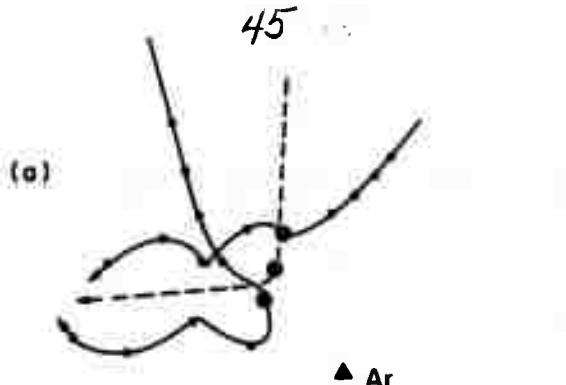


FIG. 10

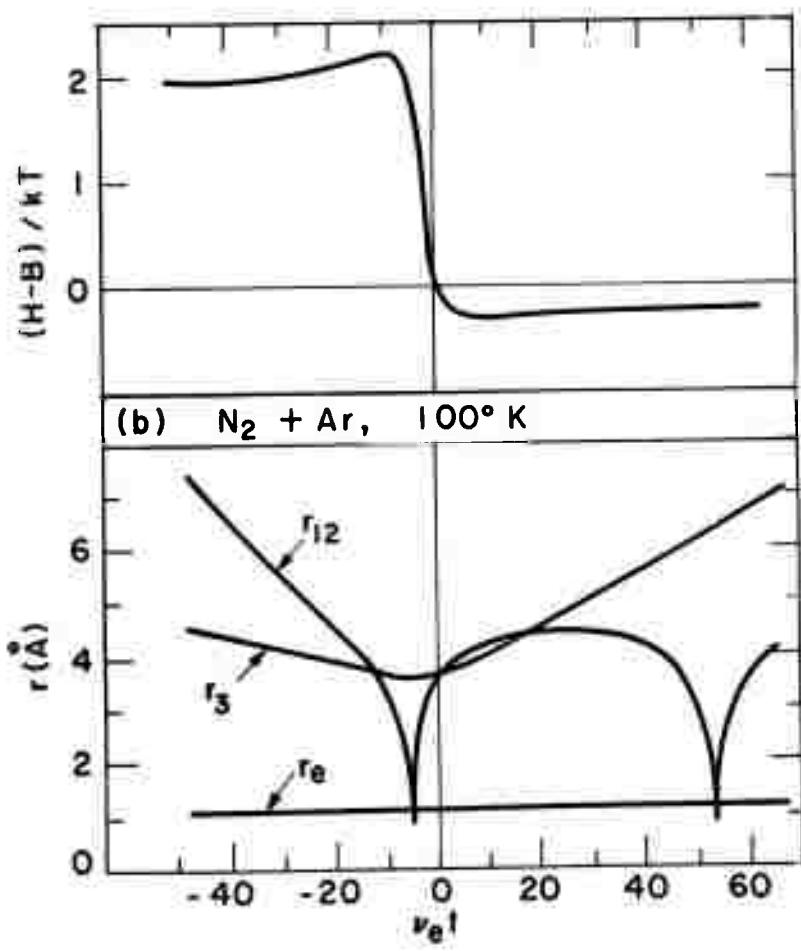
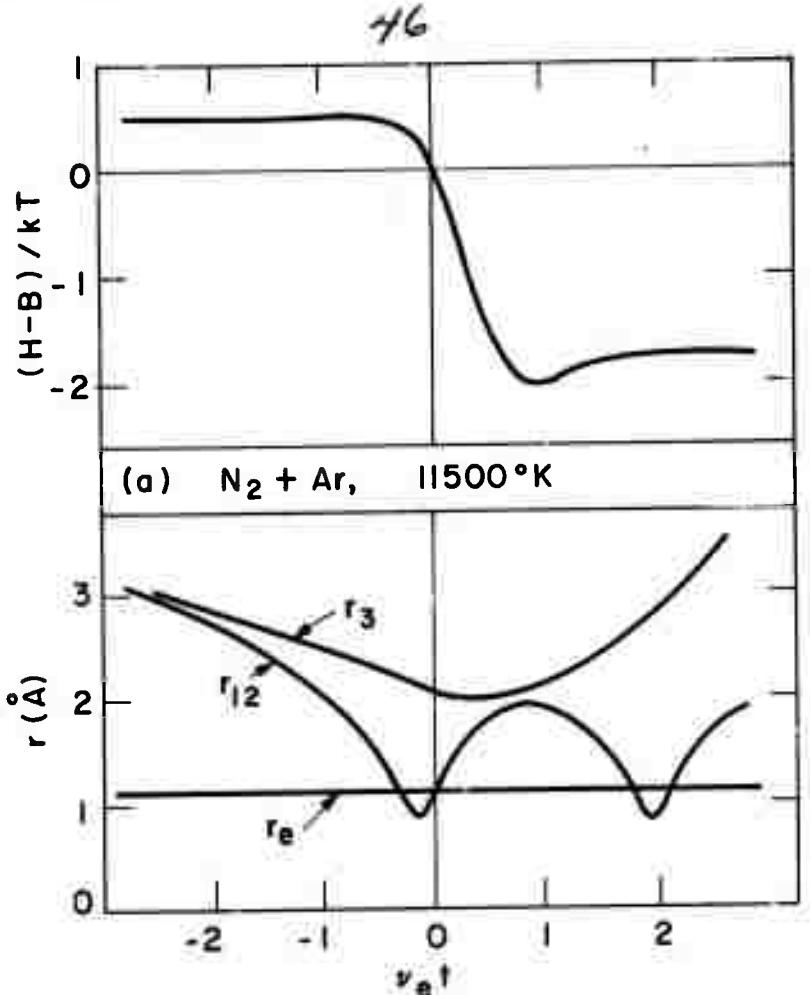
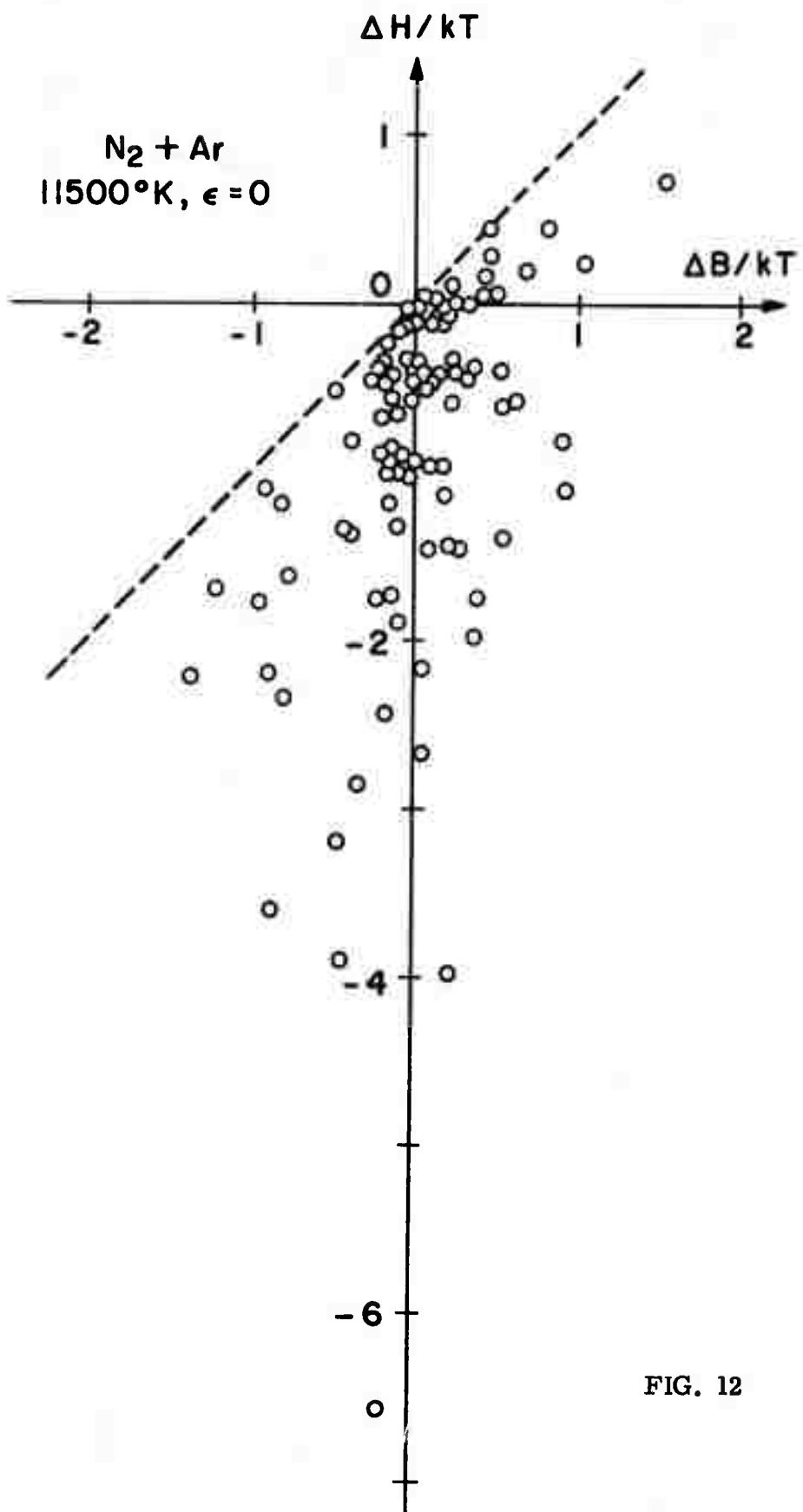


FIG. 11



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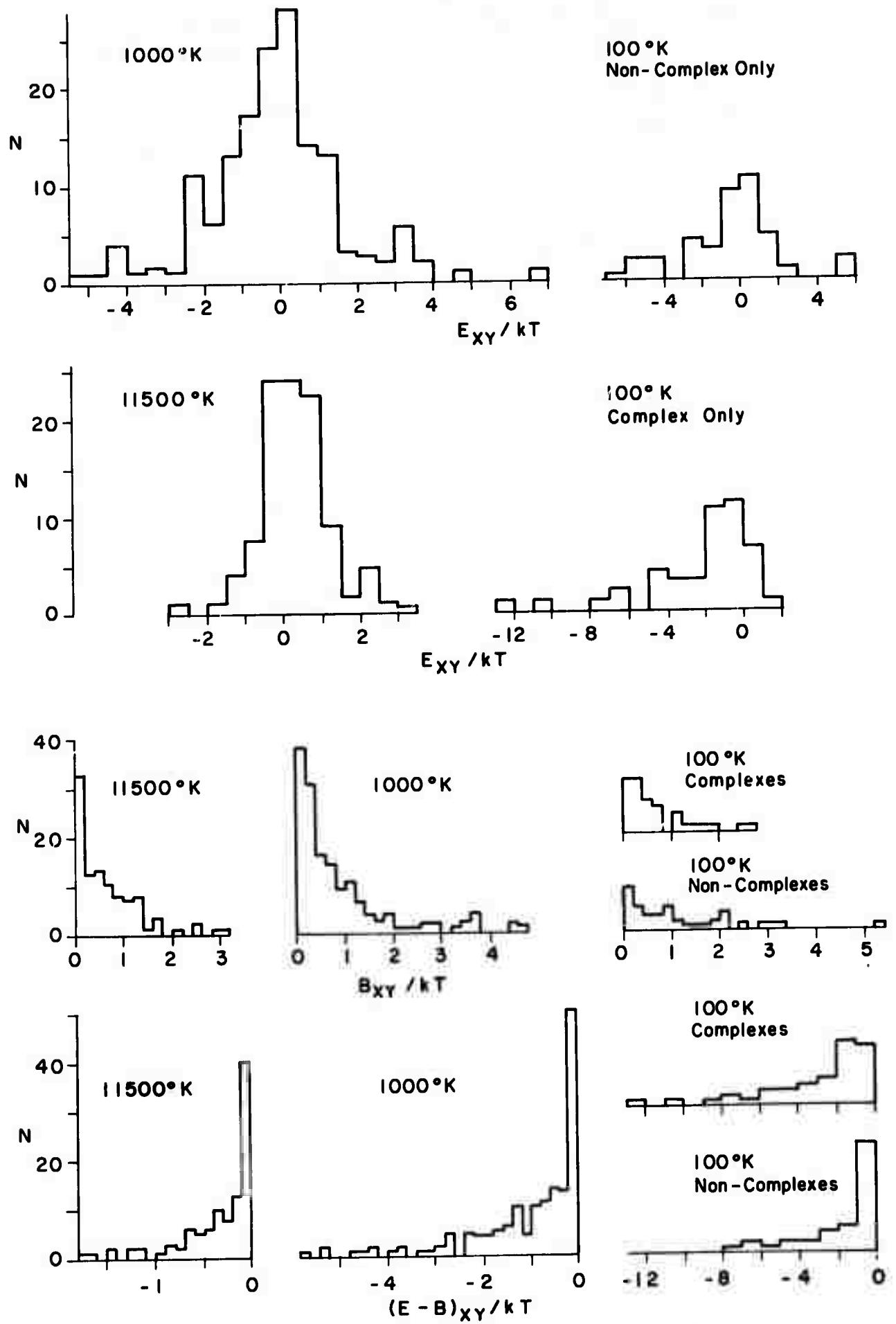


FIG. 13

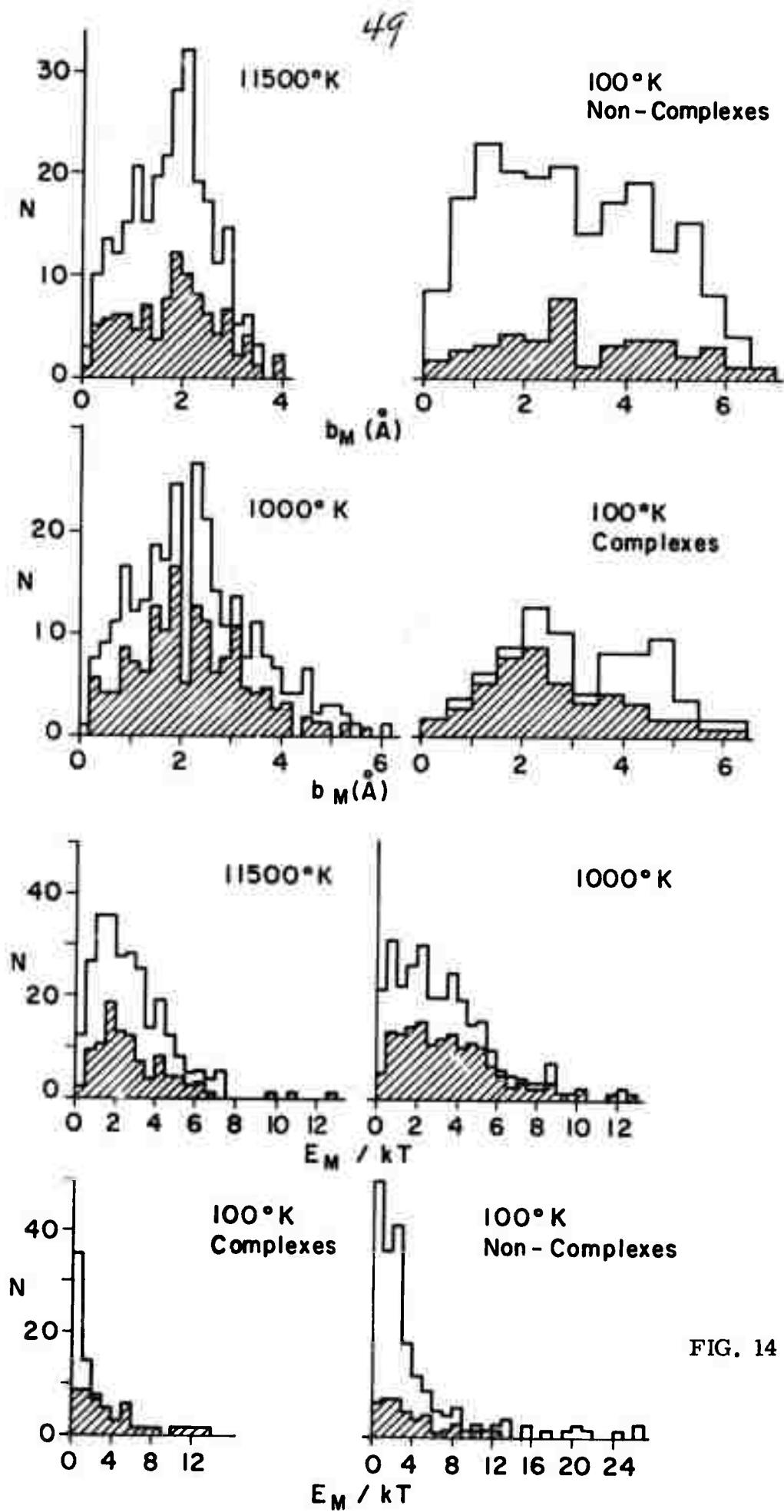


FIG. 14

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